



Influence of oxygen addition to the carrier gas on laser-induced breakdown spectroscopy measurements on aerosols



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ABSTRACT

In this work, laser-induced breakdown spectroscopy is implemented on aerosol particles for absolute concentration analysis. The aim of this work is the investigation of the effect of the bath gas used for nebulizing the aerosol. Nitrogen, air, and 50% O₂ in N₂ mixture have been chosen as carrier gasses in order to analyze the effect of oxygen addition to the gas. LIBS measurements have been carried out on aerosol particles produced from CuCl₂ 2H₂O solutions, and the 324.7 nm Cu line is considered. As a first analysis, plasma parameters, such as temperature and electron density, have been evaluated changing the carrier gas. Measurements to derive the LIBS calibration curve of the 324.7 nm Cu line are carried out in air and in N₂. The significant difference in the slope of the resulting calibration curves has to be attributed to the oxygen addition to the bath gas. To explore such behavior, time-resolved measurements of the Cu line and peak/base ratio have been performed. The presence of two competitive effects have been observed that becomes significant increasing the amount of oxygen in the carrier gas. One is the oxygen-quenching effect, already observed in the literature, and the other one is the enhancement of the Cu LIBS signal, especially at short delay times. These effects have been observed also at other Cu lines and changing the analyte source. The results are presented and widely discussed.

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1. Introduction

The analysis of aerosol particles is currently of great interest in different research areas due to the wide range of applications. Monitoring of combustion processes and their effluent waste streams, the analysis and characterization of particulate air pollution and engineered nanoparticles are only some of these applications. Several aerosol measurement techniques have been devised encompassing a broad range of operating principles. Most of these diagnostics, however, being essentially based on ex situ analysis are time consuming and require a proper sampling preparation. Atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), or mass spectrometry (ICP-MS) essentially involves collecting sample for subsequent analysis [1–3]. Hence, due also to the particular applications, there is a need to promote the development and application of suitable on-line and/or time-resolved analytical techniques. A powerful and challenging analytical technique well suited for on-line elemental analysis of aerosols is laser-induced breakdown spectroscopy (LIBS). This is an atomic emission spectroscopy technique that utilizes a laser-induced microplasma which functions as both the sample volume and the excitation source [4,5]. A pulsed laser beam is tightly focused in a particle source flow. The resulting optical breakdown decomposes and

excites all species within the plasma volume. The light emission is characterized by a continuum spectrum containing discrete atomic lines. These lines, both neutral (I) and ionic (II), and the continuum emission decay with time but persist strongly on the order of tens of microseconds. In general, the continuum spectrum decay faster than the atomic lines allowing the possibility of detecting atomic lines with a good signal-to-noise ratio by adjusting the delay and the integration time of the detector gate. However, from an analytical point of view, all the quantitative aspects of LIBS are still under study to better understand the complex nature of the laser-sample and plasma-particle interaction processes which depend on the laser pulse characteristics, sample properties, space, and time [6,7]. Applications of the LIBS technique cover a wide range of species and compounds indicating that nearly all elements of interest in aerosol analysis are readily accessible with LIBS [8–10]. Several examples of the applicability of LIBS technique to investigate and measure elemental concentration of several analytes, e.g. metals, in ambient air are reported in the literature [11–14]. Size, mass, and composition of micron and submicron aerosol particles have been evaluated [6], in most cases with the comparison and/or coupling with other techniques for aerosol characterization [12,13]. A lot of work has been done on LIBS signal processing, especially concerning the statistical analysis of single shots for detection of individual aerosol particle in dilute flow streams for atmospheric aerosol application. In this case, in fact, a proper conditional analysis has also been introduced [12,14,15], in order to take into account the non-uniform distribution of the analyte under investigation in the gas stream

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and consequently in the probe volume. As for quantitative analysis, the application of LIBS is far to be trivial. Many parameters have to be taken into account, including plasma homogeneity issues, particle size limits, and gas matrix effects [16]. Concerning the effect of the carrier gas used to generate the aerosol on LIBS signal, to our knowledge, only few works can be found in the literature. Aerosols are usually produced with purified air; however, sometimes, the use of purified N_2 could be interesting. In the work of Gleason et al. [17], the mercury atomic emission produced via breakdown has been considered and the effect of the presence of oxygen species investigated. It has been observed that the mercury emission line is selectively quenched by oxygen species, primarily O_2 and NO , formed by atoms recombination during the plasma decay. This result produces also strong effects on LIBS signal calibration. In the work of Buckley [18], different analytes have been investigated with the aim to look at the effect on the LIBS signal using N_2 or air to produce the aerosol. For Pb and Be, a reduction in the slope of the calibration curve passing from N_2 to air has been obtained due to oxygen quenching in agreement with the Hg behavior reported by Gleason et al. [17]. On the contrary, a different behavior has been exhibited by Cr. The influence of the bath gas on the LIBS signal has also been explored in the work of Pieler et al. [19] where aluminum metal measurements have been carried out.

In this work, the investigation of the influence of the carrier gas on LIBS signals is performed on aerosol particles of copper. Copper was chosen as representative analyte for environmental monitoring purpose because it can be released into the environmental air by both natural sources (wind-blown dust, decaying vegetation, forest fires, rocks weathering, and sea spray) and human activities (mining, electrical factories, metal production, construction, transportation, and phosphate fertilizer production) [20,21]. The aerosol has been produced by using alternatively purified N_2 , purified air, and 50% O_2 in N_2 mixture to nebulize and dilute/dry the aerosol droplets. In order to characterize the plasma, temperature and electron density have been evaluated. The calibration curves of 324.7 nm Cu LIBS signal have been obtained in air and N_2 . In order to explore the different slope of the resulting calibration curves, time-resolved 324.7 nm Cu LIBS measurements have been carried out in the presence of the carrier gasses under analysis. Same behavior has been obtained also for other Cu lines and changing the

analyte source. The detected differences have been discussed relatively to the chemical and thermal effects due to oxygen addition.

2. LIBS measurements

2.1. Experimental Set-up

In Fig. 1, the experimental apparatus employed for LIBS measurements is shown. A pulsed Nd:YAG laser (Continuum, 7 ns FWHM) at the fundamental wavelength (1064 nm), with 5 Hz repetition rate and 220 mJ pulse energy was used to produce the plasma by means of an 80-mm focal length lens. The plasma spectral emission was collected perpendicularly to the incident laser beam by means of two plano-convex lenses (focal length = 100 and 75 mm) onto an optical fiber (3 mm diameter) coupled with the detection unit. The latter consists of a Czerny-Turner spectrograph (Shamrock 303i) equipped with a turret of three gratings, and coupled with an intensified charge coupled device ICCD (iStar 321 T, Andor Technology) camera. For these measurements, the high-resolution grating (1200 grooves/mm) resulting in 0.113 nm resolution was used. The intensified CCD detector was synchronized with the Q-switch laser in order to change the delay and the integration width of the detector gate.

LIBS measurements were performed directly in the aerosol sample chamber, that is, a stainless steel six-ways chamber properly equipped with optical windows. Aerosol particles were produced from nebulized solutions of $CuCl_2 \cdot 2H_2O$ in ultra-purified deionized water. The particle source stream was generated using a constant output atomizer (TSI model 3075), which allows us to obtain fine droplets of about 300 nm. The droplets stream was introduced into a mixing/drying section. Here the uniform carrier co-flow gas flowing around the nebulizer output permitted to facilitate droplets vaporization via mass diffusion of water to the surrounding gas and to produce a fine dispersion of metallic salt. The resulting dried particles in the aerosol stream were carried by the co-flow gaseous stream into the sample chamber.

Knowing the droplet dimension, the solution concentration, and the salt density, the size of the dried particles was calculated to range between 14 and 30 nm. Uniform aerosol with a reasonable number of

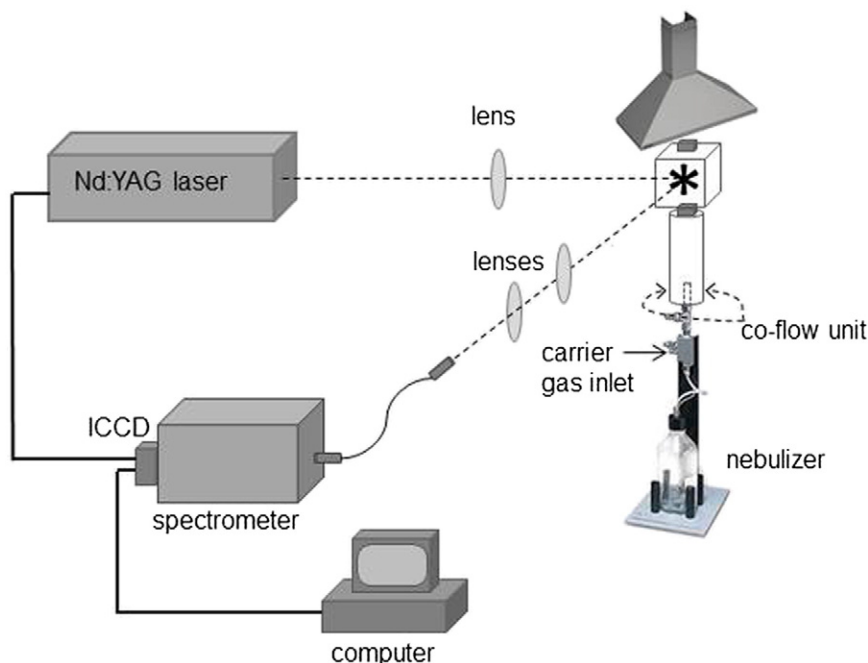


Fig. 1. Experimental set-up.

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